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Structure of Racemic Dicarbonyl(6-trifluoroacetylcarvonato)iridium(I)

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Abstract. Dicarbonyl(5-isopropenyl-2-methyl-6-trifluoroacetyl-2-cyclohexen-1-onato)iridium(I), $[\mathrm{Ir(CO)_2(C_{12}H_{12}F_3O_2)}]$, $M_r = 493\cdot4$, monoclinic, $P2_1/c$, $a = 8\cdot193$ (2), $b = 19\cdot114$ (4), $c = 9\cdot743$ (2) Å, $\beta = 93\cdot250$ (5)°, $V = 1523\cdot3$ Å^3, $Z = 4$, $D_x = 2\cdot151$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0\cdot71069$ Å, $\mu = 8\cdot468$ mm^{-1}, $F(000) = 928$, $T = 298$ K. Final $R = 0\cdot053$ for 2224 independent reflections $[F_o > 3\sigma(F_o)]$. The unit cell contains two heterochiral dimeric entities of dicarbonyl(6-trifluoroacetylcarvonato)iridium(I) (1), with an Ir–Ir distance of 3·290 (1) Å.

Introduction. The propensity of four-coordinate square-planar d^8 transition-metal compounds, *e.g.* dicarbonyl(2,4-pentanedionato)rhodium(I) [(CO)$_2$-Rh(acac)] (Bailey, Coates, Robertson, Bonati & Ugo, 1967) or $\mathrm{K_2[Pt(CN)_4]Cl_{0\cdot32}(H_2O)_{2\cdot6}}$ (Krogmann, 1969) to form one-dimensional metal chains in the solid state is well established. It has previously been demonstrated that the presence of chiral β-diketonate ligands in the inner coordination sphere of the d^8 metal ions Rh$^{\mathrm{I}}$ or Ir$^{\mathrm{I}}$ may efficiently control the extent and mode of molecular stacking in the solid state. Thus, enantiomerically pure dicarbonyl[(1*R*)-3-trifluoroacetylcamphorato]-rhodium(I) crystallizes as a yellow solid being devoid of molecular stacking while the racemate forms dichroic crystals in which the Rh atoms are linked along a distorted one-dimensional metal chain (Schurig, 1981).

While racemic dicarbonyl(3-trifluoroacetylcamphorato)iridium(I) is isomorphous with the rhodium compound, racemic dicarbonyl(3-heptafluorobutanoylcamphorato)iridium(I) is devoid of molecular stacking and only homochiral dimers (Ir–Ir 3·159 Å) are observed (Pille, 1985).

To probe the influence of steric bulk on molecular association in the solid state the bicyclic camphor moiety has been replaced by the monocyclic carvone moiety. Thus, the chelate dicarbonyl(6-trifluoroacetylcarvonato)iridium(I), containing an extended conjugated planar entity, has been prepared and its crystal structure is described here.

Experimental. Prepared from [Ir(cod)Cl]$_2$ (cod = 1,5-cyclooctadiene) with the sodium salt of racemic 6-trifluoroacetylcarvone [(5*R*/5*S*)-5-isopropenyl-2-methyl-6-trifluoroacetyl-2-cyclohexen-1-one] under a N$_2$ atmosphere in diethyl ether, followed by bubbling of CO through the filtered reaction mixture. Sublimation of the residue at 333 K/1·33 Pa and recrystallization from *n*-hexane yielded brown crystals. The exact preparation procedure will be described elsewhere (Scheer, 1990).

A single crystal with the approximate dimensions 0·07 × 0·15 × 0·4 mm was used for data collection. Lattice constants were determined from 25 reflections in the range $12 \leq \theta \leq 15°$ on a Philips PW1100/15 diffractometer. A total of 2921 reflections were measured with the ω-scan technique (hkl, $\bar{h}kl$; $-11 \leq h \leq 11$, $0 \leq k \leq 26$, $0 \leq l \leq 13$; $1\cdot5° \leq \theta \leq 30°$). Three standard reflections measured every 4 h showed constant intensities. The data were corrected for Lorentz and polarization effects; numerical absorption correction (transmission factors 0·30–0·56) leading to 2224 unique reflections with $F_o > 3\sigma(F_o)$ ($R_{\mathrm{int}} = 0\cdot050$). The structure was solved by direct methods with *SHELXS*86 (Sheldrick, 1986). Refinement on F with anisotropic parameters and H atoms in geometrically calculated positions using *SHELX*76 (Sheldrick, 1976) converged at $R = 0\cdot0527$, $wR = 0\cdot0399$, $w = k[\sigma(F_o)^2]^{-1}$, k determined by least squares, max. shift/e.s.d. in final cycle < 1, extinction correction as in *SHELX*76: $1\cdot14 \times 10^{-3}$, 206 parameters, max. residual electron density 1·34 e Å^{-3}. Since the H atoms at C(10) cannot be positioned geometrically with *SHELX*76, they are not given in Table 1, in which the atomic parameters

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Table 1. *Atomic positional and equivalent isotropic thermal parameters for* (1)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}(Å^2)
Ir(1)	0·35734 (6)	−0·01278 (2)	0·60951 (5)	0·0463 (1)
C(1)	0·198 (2)	−0·0371 (6)	0·482 (1)	0·056 (5)
O(1)	0·096 (1)	−0·0532 (5)	0·402 (1)	0·086 (5)
C(2)	0·318 (2)	0·0794 (7)	0·574 (1)	0·058 (5)
O(2)	0·293 (1)	0·1378 (5)	0·5533 (9)	0·080 (4)
O(3)	0·5289 (8)	0·0083 (4)	0·7576 (7)	0·051 (3)
C(3)	0·618 (1)	−0·0351 (6)	0·833 (1)	0·046 (5)
C(4)	0·731 (1)	0·0016 (5)	0·939 (1)	0·053 (5)
C(5)	0·745 (2)	0·0799 (6)	0·926 (1)	0·067 (6)
C(6)	0·794 (1)	−0·0347 (6)	1·042 (1)	0·053 (5)
C(7)	0·766 (2)	−0·1113 (6)	1·058 (1)	0·062 (6)
C(8)	0·738 (1)	−0·1494 (5)	0·919 (1)	0·048 (5)
C(9)	0·900 (1)	−0·1630 (6)	0·852 (1)	0·054 (5)
C(10)	0·956 (2)	−0·1254 (7)	0·750 (1)	0·065 (6)
C(11)	0·993 (2)	−0·2234 (6)	0·914 (2)	0·081 (6)
C(12)	0·613 (1)	−0·1089 (5)	0·826 (1)	0·042 (4)
C(13)	0·503 (1)	−0·1407 (6)	0·738 (1)	0·046 (5)
C(14)	0·491 (2)	−0·2202 (7)	0·735 (1)	0·064 (6)
F(1)	0·384 (1)	−0·2423 (4)	0·6390 (8)	0·100 (4)
F(2)	0·631 (1)	−0·2515 (4)	0·7136 (8)	0·083 (4)
F(3)	0·440 (1)	−0·2469 (4)	0·8506 (8)	0·085 (4)
O(4)	0·397 (1)	−0·1138 (4)	0·6514 (7)	0·057 (4)

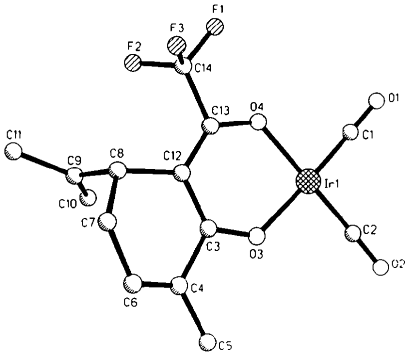

Fig. 1. Molecular structure of (1).

for (1) are listed.* The positions of the two missing H atoms could also not be located in the final difference map.

Scattering factors for Ir^0 were taken from *International Tables for X-ray Crystallography* (1974), others as supplied by *SHELX*. Diagrams were drawn with *SHELXTL-Plus* (Sheldrick, 1987).

Bond distances and angles are given in Table 2. Fig. 1 shows the molecular structure of (1) and Fig. 2 contains a stereoscopic view of the unit cell (view along [001]).

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Ir(1)—C(1)	1·81 (2)	C(7)—C(8)	1·54 (2)
Ir(1)—C(2)	1·82 (2)	C(8)—C(9)	1·53 (2)
Ir(1)—O(3)	1·997 (7)	C(8)—C(12)	1·54 (2)
Ir(1)—O(4)	1·996 (8)	C(9)—C(10)	1·33 (2)
C(1)—O(1)	1·15 (2)	C(9)—C(11)	1·49 (2)
C(2)—O(2)	1·15 (2)	C(12)—C(13)	1·35 (2)
C(3)—O(3)	1·30 (2)	C(13)—C(14)	1·52 (2)
C(3)—C(4)	1·52 (2)	O(4)—C(13)	1·28 (2)
C(3)—C(12)	1·41 (2)	F(1)—C(14)	1·32 (2)
C(4)—C(5)	1·51 (2)	F(2)—C(14)	1·32 (2)
C(4)—C(6)	1·30 (2)	F(3)—C(14)	1·33 (2)
C(6)—C(7)	1·49 (2)	Ir(1)—Ir(1)*	3·290 (1)
C(1)—Ir(1)—C(2)	90·3 (6)	C(8)—C(9)—C(10)	125 (2)
C(1)—Ir(1)—O(4)	89·7 (4)	C(8)—C(9)—C(11)	113 (1)
C(1)—Ir(1)—O(3)	176·1 (4)	C(10)—C(9)—C(11)	122 (2)
C(2)—Ir(1)—O(4)	178·8 (5)	C(3)—C(12)—C(8)	117·2 (8)
C(2)—Ir(1)—O(3)	93·0 (3)	C(3)—C(12)—C(13)	119·7 (9)
O(4)—Ir(1)—O(3)	87·0 (3)	C(8)—C(12)—C(13)	123·0 (9)
O(1)—C(1)—Ir(1)	179 (2)	O(4)—C(13)—C(12)	130 (12)
O(2)—C(2)—Ir(1)	179·1 (9)	O(4)—C(13)—C(14)	110·3 (9)
C(3)—O(3)—Ir(1)	128·8 (7)	C(12)—C(13)—C(14)	120·0 (9)
O(3)—C(3)—C(12)	126·5 (8)	F(1)—C(14)—F(2)	107 (1)
O(3)—C(3)—C(4)	112·9 (9)	F(1)—C(14)—F(3)	105 (2)
C(4)—C(3)—C(12)	120·6 (8)	F(1)—C(14)—C(13)	112 (1)
C(5)—C(4)—C(6)	124·4 (9)	F(2)—C(14)—F(3)	106 (1)
C(3)—C(4)—C(6)	118·5 (9)	F(2)—C(14)—C(13)	114 (2)
C(3)—C(4)—C(5)	116·6 (9)	F(3)—C(14)—C(13)	113·0 (9)
C(4)—C(6)—C(7)	123·2 (9)	C(13)—O(4)—Ir(1)	128.2 (7)
C(6)—C(7)—C(8)	112·8 (8)	Ir(1)*—Ir(1)—C(1)	96·0
C(7)—C(8)—C(9)	11·4 (9)	Ir(1)*—Ir(1)—C(2)	81·8
C(7)—C(8)—C(12)	109·9 (8)	Ir(1)*—Ir(1)—O(3)	86·7
C(9)—C(8)—C(12)	113·5 (8)	Ir(1)*—Ir(1)—O(4)	82·5

* Atom on the position $-x$, $-y$, $-z$ related by the inversion centre.

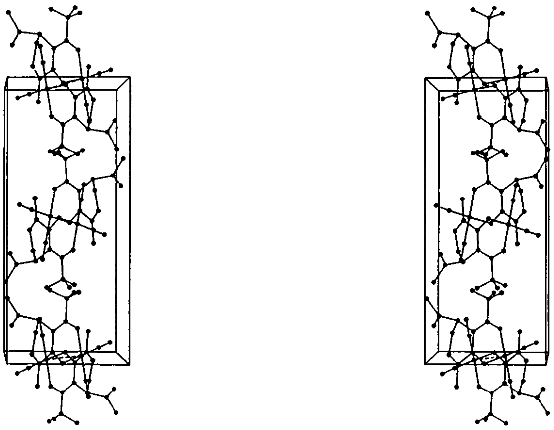

Fig. 2. Stereoscopic view of the unit cell (view along [001]).

Discussion. The Ir atom in (1) is surrounded by two O atoms of the 6-trifluoroacetylcarvonate ligand and by two C atoms of the carbonyl groups in an essentially square planar geometry. The average Ir—C distance is 1·816 (13) Å and the average Ir—O distance is 1·997 (8) Å. These distances are comparable with those reported for iridium(I) complexes with related β-diketonate ligands (Pille, 1985). As

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52797 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

expected, the extended conjugated ketoenolate ligand is nearly planar with the bulky isopropenyl group directed outwards from the plane. Surprisingly, no linear metal chain is formed in the solid state, but only dimeric entities are observed. The intermolecular Ir–Ir distance within the dimer is 3·29 Å, indicating a weak metal–metal interaction, and may be compared with the values for the one-dimensional metal chains in dicarbonyl(2,4-pentanedionato)iridium(I) (Ir–Ir 3·20 Å) (Pitt, Monteith, Ballard, Collman, Morrow, Roper & Ulkü, 1966) or in racemic dicarbonyl(3-trifluoroacetylcamphorato)iridium(I) (Ir–Ir 3·34 Å) (Pille, 1985). In contrast to racemic dicarbonyl(3-heptafluorobutanoylcamphorato)iridium(I) the dimers are not formed from homochiral complexes (*R*/*R* or *S*/*S*) but from heterochiral complexes (*R*/*S*). The reason for the failure of the title compound to undergo molecular stacking in the solid state is unknown at present.

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Structure of $Au_2[S_2CN(C_2H_5)_2]_2$, Bis(diethyldithiocarbamato)digold(I)

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Abstract. Bis(μ-*N*,*N*-diethyldithiocarbamato-*S*,*S*′)-digold(I), [$Au_2(C_5H_{10}NS_2)_2$], $M_r = 690·45$, tetragonal, $I4_1/a$, $a = 18·060$ (3), $c = 22·914$ (3) Å, $V = 7473·1$ (18) Å^3, $D_x = 2·45$ g cm^{-3}, $Z = 16$, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 160·8$ cm^{-1}, $F(000) = 5054$, $T = 295$ K, final $R = 0·037$ and $wR = 0·053$ using 163 parameters and 1951 reflections with $F_o > 3\sigma F_o$. The structure consists of discrete dimers each containing two Au atoms bridged by two diethyldithiocarbamate ligands. The intramolecular Au—Au distance is 2·782 (1) Å, with Au—S distances ranging from 2·28 to 2·30 Å. The packing of the dimeric units produces linear chains of Au atoms containing the shortest intermolecular Au—Au distance yet found in these dithiocarbamate digold(I) compounds [3·004 (1) Å].

Introduction. Our recent success in the preparation of dinuclear gold(II) ylide compounds containing thiolate ligands (Heinrich, 1987; Heinrich & Fackler, 1986) and in the preparation of a series of dinuclear Au^{I} and Au^{II} compounds bridged by 1,1-dicyano-2,2-ethylenedithiolate (i-mnt) (Khan, Fackler, King, Wang & Wang, 1988; Khan, Wang, Heinrich & Fackler, 1988) has prompted us to re-examine the chemistry of the dithiocarbamate dimers of gold(I). Dinuclear Au^{I} dithiocarbamate complexes have been studied in the past; the dipropyldithiocarbamate (Hesse & Jennische, 1972) and dibutyldithiocarbamate (Jennische, Anacker-Eickhoff & Wahlberg, 1975) complexes have been structurally characterized. In the solid state these compounds are found to stack so as to form linear gold chains with short intra- and intermolecular Au—Au distances. Although the structural characterization of a dinuclear Au^{II} system containing an Au—Au bond has not been achieved, Burmeister and co-workers have observed these species at low temperatures (Calabro, Harrison, Palmer, Moguel, Rebbert & Burmeister, 1981). As part of our studies we have been investigating the luminescence of Au systems which contain either Au—Au bonds or linear chains of Au atoms in

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